An Initiating Mechanism of Color Formation and Decomposition in Polyvinyl Chloride

SVEN SÖNNERSKOG

A-B Svenskt Konstsilke, Borås, Sweden

The thermal instability of polyvinyl chloride, prepared in emulsion systems, is related to the presence of peroxides, formed during the polymerization process, or later, by autoxidation. The rate of color formation and decomposition is preferably studied in pyridine below 100°C. Redox systems, where the polymer takes part as an active component, are effective inhibitors of discoloration and degradation. Graft copolymers can be prepared by a seeding technique, based upon the same principle.

Polymerization of vinyl chloride is usually carried out in emulsion systems. The reaction takes place in water, containing ammonium or sodium salts of higher, saturated fatty acids. The aqueous phase is saturated with monomer under pressure at moderate temperatures (40—50°C). Persulphate ions are the preferred initiators. Sulphate ion radicals are generated by thermal dissociation, followed by diffusion into soap micelles, where solubilized monomer enters into reaction. The general picture of the kinetic scheme at steady state conditions is well-known from the fundamental work of Smith and Ewart [1,2].

The degree of conversion of monomer into polymer may be varied by release of pressure at different times of reaction. This is actually used in practice as a versatile method influencing upon the solubility characteristics of the final polymer; other working variables, such as added amounts of initiator, soap and modifiers being unconsidered.

A critical state arises in the polymerising system when remaining monomer is suddenly removed. Growing polymer radicals have to find a way of deactivation or propagation. Traces of molecular oxygen may act as comonomer: *

$$R \cdot + O_2 = R{-}O{-}O \cdot$$

---
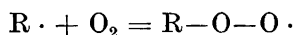
* The occurrence of an induction period in vinyl chloride polymerization indicates formation of peroxide radicals at this early stage of the process, but this does not exclude the presence of oxygen at high degrees of conversion, as monomer is preferably added continually to the reacting system.

especially when the concentration of vinyl chloride is low. Radicals, trapped in the polymer particle, will react in the same way, when exposed to air at (spray) drying or grinding operations. Deactivation occurs by hydrogen abstraction from the surrounding medium. The net result is a polymeric hydroperoxide. High degree of stability and bad accessibility may cooperate to render its detection difficult by standard reagents.

The dry, purified polymer is soluble in pyridine at room temperature, or slightly above, at moderate degrees of polymerization. Such a solution remains colorless at 0—5°C in the absence of light, but discoloration rapidly takes place in sunlight or merely by heating, even in an inert atmosphere. The following changes of color are observed at 100°C (Table 1).

Table 1. Color formation in a solution of polyvinyl chloride in pyridine at 100°C. Concentration of solute: 10^{-2} g · ml^{-1}.

Time of heating, min	Color
0	Water white
10	Pale brown
25	Pale red brown
145	Red brown
300	Deeply red
330	Dusky brown
Blank of solvent after 330 min : water white	

The color changes indicated above are accompanied by a gradually decreased solubility, easily seen by cooling back to room temperature, when a gel is obtained from deeply colored solutions. This sol-gel transformation is reversible within the period of heating, found in Table 1. At continued thermolysis, approximately during 10—12 h, the hot solution shows increasingly viscoelastic properties, apparently due to formation of an infinite network. The dusky brown color is further enhanced.

It deserves to be noticed that similar results are obtained when the polymer is purified by reprecipitation from dioxane or separated into two fractions by soaking in acetone. The instability in pyridine seems to be a property inherently related to molecular structure.

Identical changes of color are observed when polyvinyl chloride is milled with plasticizers at elevated temperature in the absence of stabilizers. Extensive trial and error has been a requisite of finding adequate structures of such additives. The work has partly been guided by the current opinion that stabilizers principally act as scavengers for hydrogen chloride [3–6]. This is an oversimplification, as recently pointed out [7,8], as hydrogen chloride is a secondary product from a transfer reaction between a chlorine atom and a macromolecule:

$$\sim\!\sim\!\sim\!CH_2-CHCl-CH_2-CHCl\!\sim\!\sim \;+\; Cl\cdot \;=\; HCl \;+\; \sim\!\sim\!CH_2-$$
$$CHCl-\overset{\bullet}{CH}-CHCl\!\sim\!\sim$$
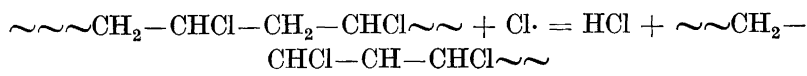
leaving the question open in what way elementary chlorine is liberated. Earlier studies on dehydrochlorination of polyvinyl chloride [7-9] suggest the existence of thermolabile chlorine-carbon bonds in special chain sections of the macromolecules, for instance at branching units (chlorine bonded to a tertiary carbon atom) or in the vicinity of unsaturated end groups. These groups would be formed when termination occurs by disproportionation or by chain transfer to monomer. Many explanations merely rest on the incidental presence of initiator residues in the primary polymer particles. Such impurities dissociate on heating into free radicals and initiate degradation and decomposition by a chain reaction.

In the opinion of the writer no imperfections of these kinds are indispensable to explain the thermal instability of polyvinyl chloride, prepared in emulsion systems, as the presence of (hydro) peroxides can be varified experimentally in a very simple manner. Even a peroxide of unusual stability would be decomposed in a basic medium as pyridine by the formation of a redox system with said peroxide as active component. This can be done in many ways, but it is exceedingly important to find such coreactants that deactivate the released radicals without generation of a new population attacking the polymer. It also deserves to be noticed that free radicals and elementary chlorine mostly show identical type reactions, why a distinction between primary and secondary steps would be solely obtained at such a low reaction temperature, where thermal dissociation of $C-Cl$ bonds is insignificant. Fortunately many redox systems are worked out with a view of acting at room temperature or below. Table 2 shows some reduction activators, inhibiting color formation in solu-

Table 2. Inhibitors of color formation in solutions of polyvinyl chloride in pyridine.

Coreactant(s)	Added amount to 1 g polymer	Suggested type reactions
$H_2N-OH \cdot HCl$	0.01—0.1 g	$ROOH \rightarrow RO \cdot + HO \cdot$ $HO \cdot + H_2N-OH \rightarrow H_2O + H\dot{N}-OH$ $RO \cdot + H_2N-OH \rightarrow ROH + H\dot{N}-OH$ $2\ H\dot{N}-OH \rightarrow N_2 + 2\ H_2O$
H_2N-NH_2 $+ FeCl_2$	0.01—0.1 g 10 mg	$ROOH \rightarrow RO \cdot + HO \cdot$ $Fe^{2+} + HO \cdot \rightarrow Fe^{3+} + HO:^-$ $RO \cdot + H_2N-NH_2 \rightarrow ROH + H\dot{N}-NH_2$ $Fe^{3+} + H_2N-NH_2 \rightarrow Fe^{2+} + H\overset{+}{\cdot} + H\dot{N}-NH_2$ $H^+ + HO:^- \rightarrow H_2O$ $2\ H\dot{N}-NH_2 \rightarrow 2\ NH_3 + N_2$
$H_2N-NH_2 \cdot H_2O$	0.1 g	$N_2H_4 \cdot H_2O \rightleftharpoons H_2N-NH_3^+ + HO:^-$ $ROOH \xrightarrow{\text{(HO:}^-\text{)}} RO \cdot + HO \cdot$ $RO \cdot + N_2H_4 \rightarrow ROH + \dot{N}_2H_3$ $HO \cdot + N_2H_4 \rightarrow H_2O + \dot{N}_2H_3$ $2\ \dot{N}_2H_3 \rightarrow 2\ NH_3 + N_2$

tions of polyvinyl chloride in pyridine below 100°C. Inhibition has been considered as satisfactory when no color formation is visible during the schedule of observation, used in Table 1.

Several reducing agents behave as strong retarders of color formation and gelation. Paraformaldehyde, hydroquinone and p-hydroxybenzoic acid are a few of them. Classical inhibitors of vinyl polymerization, nitrobenzene and picric acid, show a similar effect. Unsaturated compounds, known to polymerize in a neutral aqueous medium by initiation of radicals, inhibit the later steps of the color formation cycle (red and dusky brown). This is especially valid for N,N'-methylene-bis(acrylamide).

The prehistory of the polymer is rather important, quite apart from the very method of preparation. It has been repeatedly observed that technical grades of polyvinyl chloride with a very low particle size are able to oxidise p-aminophenol, metol and pyrogallol at room temperature in the absence of air (suspension in methanol-water-reagent). A reprecipation from pyridine reduces the rate of oxidation, — indicated by the brown/black color in the liquid — but this improvement is gradually lost by repeated drying in air. Hydroperoxydation of polyvinyl chlroide would seem to be partly reversible.

Present experience on the properties of polyvinyl chloride (emulsion type) supports the idea that it might serve as an initiator of vinyl polymerization, provided the reaction medium is selected with care. This was proved by making a graft copolymer with acrylonitrile according to a "seeding" technique. The reacting mixture consisted of:

Polyvinyl chloride (5 g), dispersed in 500 g water,
Antarox G 100 (a nonionic detergent, 1 g)
Sodium pyrosulphite (1 g) and ferrous chloride (0.1 g)
Acrylonitrile (25 g)
Temp. of reaction: 32°C, time of reaction: 240 min, rate of stirring: 50 rpm.

Yield of pure, dry copolymer: 22 g.

It was easily verified that a true graft copolymer had been produced. Contrary to homopolymers of acrylonitrile dissolution can be carried out at 15—20°C, using only pyridine as solvent. Such a solution shows a very low viscosity and phase separation takes place on heating. Stable solutions are found in dimethyl formamide and dimethyl sulfoxide.

The high reactivity of polyvinyl chloride in the presence of reduction activators and a comonomer emphasises its character of peroxide or polymer radical. The inherent thermal instability of technically produced material is self-evident from this point of view. It also explains why a minor amount of (elementary) chlorine is stripped from the polymer already during its synthesis. After a long induction period due to oxygen, polymerization sets in at a rate far exceeding that working at standard conditions in an inert atmosphere. Polymeric peroxides at arbitrary degrees of polymerization are apparently decomposed into free radicals. Their primary constitution may be written

$$\sim\!\sim\!\sim\!\sim\!CH_2-CH-O\cdot \;\rightarrow\; \sim\!\sim\!\sim\!CH_2-CH-O\cdot \,+\, Cl\cdot$$
$$\underset{Cl}{|}$$
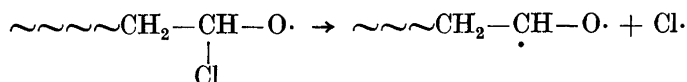
Such a radical would be easily deactivated, if its reactivity is too low to initiate propagation, as the chlorine atom is in a labile position, compared to a regular sequence. Final polymer would show the presence of carbonyl groups in its infrared spectrum. This has been confirmed [9].

REFERENCES

1. Smith, W. V. and Ewart, R. H. *J. Chem. Phys.* **16** (1948) 592.
2. Smith, W. V. *J. Am. Chem. Soc.* **70** (1948) 3695.
3. Drusedow, D. and Gibbs, C. F. *Modern Plastics* **30** (1953) 123.
4. Arlman, E. J. *J. Polymer Sci.* **12** (1954) 543.
5. Fox, V. W., Hendricks, J. G. and Ratti, H. J. *Ind. Eng. Chem.* **41** (1949) 1774.
6. Smith, H. V. *Brit. Plastics* **25** (1952) 304.
7. Winkler, D. E. *J. Polymer Sci.* **35** (1959) 3.
8. Stromberg, R. R., Strauss, S. and Achhammer, B. G. *J. Polymer Sci.* **35** (1959) 355.
9. Baum, B. and Wartman, L. H. *J. Polymer Sci.* **28** (1958) 537.